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An Investigation of Extinguishment by Thermal Agents Using Detailed Chemical Kinetic Modeling of Opposed Jet Diffusion Flames

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Abstract

Thermal fire-fighting agents are being investigated as potential replacements for halons which can no longer be manufactured due to their deleterious effects on stratospheric ozone. This work describes a detailed chemical kinetic modeling study of methane planar opposed jet laminar diffusion flames burning in air diluted with various thermal agents. Extinction conditions are characterized as a function of agent concentration. Comparison of the calculated results for burning in nitrogen-diluted air with literature values for the extinguishing concentration allows the corresponding maximum flame temperature at extinguishment to be estimated as 1550 K. By applying this criterion, extinguishing concentrations are calculated for argon, helium, carbon dioxide, and water vapor. Calculated values are shown to be in good agreement with measurements in cup burners using heptane fuel. Surrogate agents having non physical behaviors have been used to characterize particular aspects of flame extinguishment by thermal agents. It is shown that dilution effects result from passage of oxygen through the flame front and that these effects should be accounted for when estimating the amount of a particular thermal agent required to extinguish a flame. By the use of a surrogate agent which absorbs heat by unimolecular reaction, it is demonstrated that the physical location of the heat extraction relative to the flame front does not modify the effectiveness of a thermal agent as long as the agent is subsequently convected into the flame zone.

1. Introduction

The manufacture of halons which have been widely used in fire extinguishing systems was banned in 1994 due to their deleterious effect on stratospheric ozone. As part of a coordinated effort to identify suitable halon replacements, the National Institute of Standards and Technology is investigating whether highly effective thermal agents are feasible. Thermal agents are defined as those which obtain their effectiveness solely by heat extraction and dilution. A great deal is known about the effects of thermal agents on flames. The paper by Sheinson et al. provides a good introduction [1]. There are a number of endothermic physical processes which can extract heat from a gaseous flame zone, thus lowering the temperature and ultimately leading to flame extinguishment. These include simple heating (i.e., heat capacity) of an agent, phase changes such as vaporization of a liquid or sublimation of a solid, endothermic molecular decomposition, and simple dilution. The flame temperature is also expected to be a function of the thermal diffusivity of an agent.

This paper describes a detailed chemical-kinetic modeling investigation of methane planar opposed-jet laminar diffusion flames (POJLDFs) burning in air diluted with various thermal agents

which is designed to provide an improved understanding of the extinguishment of fires by thermal agents. An internal report is available which summarizes the kinetic modeling in more detail and also includes the results of an extensive data base search of potential thermal agents and modeling results for the effectiveness of thermal agents in cooling liquid surfaces [2].

2. Detailed Chemical Kinetic Modeling

A series of methane POJLDFs have been calculated as a function of the counterflowing fuel and oxidizer velocities at the burner exits (assumed to have equal magnitudes, hereafter referred to as the *exit velocity*) and the concentration of various thermal agents added to the air side. For each concentration of added agent, an extinction condition is identified corresponding to a given exit velocity. A focus of this work is the identification of the minimum concentration of an agent required to extinguish buoyancy-dominated fires. The *extinguishing concentration* is expected to correspond to a particular POJLDF extinction condition. It will be shown in this paper that the extinguishing concentration can be related to a particular maximum flame temperature, T_{max} , observed for the POJLDF at extinction.

The code Oppdif [3] developed by Sandia National Laboratories and now available commercially from Reaction Design* was used for the calculations. After reviewing the literature, the widely used methane/air mechanism developed with the support of the Gas Research Institute was chosen for the calculations. The version used was GRI-Mech 1.2 [4] which consists of 32 chemical species undergoing 177 reactions.

In order to determine the extinction behavior for a flame, a stable burning solution was first obtained using a relatively low exit velocity. The resulting solution was then used as input for a calculation with a higher exit velocity. This process was repeated until the flame went out or a solution was not obtained. By approaching the extinction exit velocity in small increments, it was possible to calculate the extinction point to within a step size of 0.01 cm/s.

3. Modeling Results

Figure 1 includes a plot of T_{max} versus exit velocity calculated for a methane/air (0% added nitrogen) POJLDF. Air is assumed to be composed of 78.1% N₂, 21.0% O₂, and 0.9% Ar by volume. As expected, T_{max} decreases with increasing exit velocity. Extinction is calculated to occur at 320.12 cm/s with $T_{max} = 1785$ K. A number of parameters have been used in the literature to characterize the effects of varying exit velocities on POJLDFs. One of these is the maximum value of the velocity gradient element, a_o , observed on the oxidizer side outside of the boundary layer with a defined as

*Certain commercial equipment, instruments, or material are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

$$a = \frac{\partial u}{\partial z}, \quad (1)$$

where z and u are the direction and velocity component normal to the flame sheet. The calculated value of $|a_o|$ for the methane flame at extinction is 509 s^{-1} , which is roughly 25% higher than measured experimentally [5,6,7]. Tanoff et al. have shown that calculated values of a_o are dependent on the detailed mechanism used [8]. In their work GRI-Mech also overpredicted a_o .

We have identified only a limited number of experimental measurements of extinguishing concentrations for methane flames burning in air diluted with thermal agents. Most are for nitrogen. Simmons and Wolfhard [9], Ishizuka and Tsuji [10], and Puri and Shesadri [11] reported extinguishing mole fractions of 0.338, 0.319, and 0.286, respectively, for various types of opposed-flow flames. Ural has recently reported an extinguishing nitrogen mole fraction of 0.271 for a coflowing methane diffusion flame [12]. For the purposes of this work we have chosen to average the two higher experimental values to obtain a mole fraction of 0.33 added nitrogen as being representative of the extinguishing concentration.

A series of calculations was performed for methane POJLDFs reacting with air containing various percentages of added nitrogen. Figure 1 shows the results. As the percentage of added nitrogen increases, the exit velocities sufficient to induce flame extinction decrease. T_{max} at extinction also decreases with increasing nitrogen concentration. Plots of T_{max} versus exit velocity become steeper with increasing nitrogen concentration.

As stated earlier, the nominal experimental extinguishing mole fraction of nitrogen is 0.33. The calculated T_{max} at extinction for this condition is 1545 K. This is close to the experimental value of 1483 K reported by Ishizuka and Tsuji [10]. Both the calculated and experimental estimates for T_{max} at extinguishment are consistent with others in the literature [1,13].

For the extinguishing concentration of nitrogen, the extinction exit velocity is calculated to be 21.42 cm/s. The corresponding value of $|a_o|$ is 27.0 s^{-1} . An important question concerning the extinction of diffusion flames is: what strain rate is appropriate to use when determining an extinguishing concentration? The only literature discussions of this point identified were presented by Hamins et al. [14] and Saso et al. [15]. These authors compared extinguishing concentrations for a variety of agents determined with cup burners fueled with heptane [14,15] and ethanol [15] with corresponding results for counterflow flames. The counterflow measurements were made over a range of exit velocities characterized in terms of global strain rates, a_g . When the agent concentrations were comparable to those which induced extinguishment in the cup burner, a_g values reported by Hamins et al. were roughly 50 s^{-1} , while Saso et al. reported a_g values of $\approx 30 \text{ s}^{-1}$. Due to use of different boundary conditions and fuels

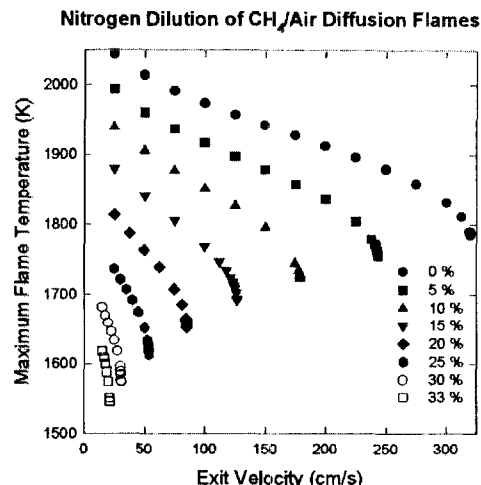


Figure 1. Maximum flame temperatures are plotted versus exit velocity for methane flames burning in air diluted by various percentages of added nitrogen.

between the current investigation and those of Hamins et al. and Saso et al., as well as the use of different definitions for the characteristic strain rates, absolute quantitative comparisons are not appropriate. However, it is clear that the characteristic strain rates are of comparable magnitude. It is important to note that the characteristic strain rates appropriate for characterizing extinguishing conditions are much lower than typically used for experimental and modeling investigations of opposed-flow diffusion flames.

It is interesting to speculate why flames subject to Earth's gravity apparently cannot be sustained below a well defined characteristic strain rate. The most likely reason is that buoyancy effects place a limit on the lowest characteristic strain rates present in the flame. Buoyancy always accelerates hot combustion gases relative to the cold oxidizer, with the result that flame surfaces are subject to nonzero strain rates. The results of Hamins et al. [14] and Saso et al. [15] along with the current findings suggest this strain rate limit is on the order of a few tens of inverse seconds.

As already noted, no additional measurements of extinguishing concentrations for other thermal agents added to methane/air diffusion flames were identified. However, Ishizuka and Tsuji did make measurements for methane burning in an artificial "air" consisting of 21% oxygen and 79% argon [10]. This "air" was diluted with argon until extinguishment occurred. The extinguishing mole fraction for added argon was 0.543. T_{max} at extinguishment was 1443 K, or roughly 40 K less than for standard air diluted with nitrogen. A series of calculations for methane flames burning in argon "air" diluted with argon were carried out in the present work. A flame burning in argon "air" with 54% added argon is calculated to undergo extinction with $T_{max} = 1473$ K and an exit velocity of 15.9 cm/s. If one simply assumes that extinguishment occurs for the same T_{max} , i.e., 1550 K, as for the nitrogen-diluted air flame, an estimate for the required concentration of added argon of 52% is obtained. This is only 4% less than the experimental value. Thus, assuming that flame extinguishment occurs for the agent concentration necessary to reduce T_{max} at extinction to 1550 K should provide an excellent estimate for the mole fraction of an arbitrary thermal agent required to extinguish a fire. This approach was adopted for estimating extinguishing concentrations.

POJLDF calculations have been used to estimate the required extinguishing concentrations for methane burning in air diluted with Ar, He, CO₂, and H₂O. Water is assumed to be a gas even though at room temperature the required concentrations in air correspond to supersaturated conditions. Each of these gases is expected to act primarily as a thermal agent. The resulting plots (not shown) of T_{max} versus exit velocity exhibit trends similar to those for nitrogen shown in Figure 1. Estimates for extinguishing concentrations are tabulated in Table 1.

As already discussed, the only experimental values of extinguishing concentrations for thermal agents added to air we have identified for methane diffusion flames are for nitrogen. Cup burner determinations of extinguishing concentrations using heptane as fuel have been reported for some of these agents by Sheinson et al. [1], Babb et al. [13], Hamins et al. [16], Moore et al. [17], and Saito et al. [18]. These are summarized in Table 1. The maximum difference between values calculated for methane and the experimental values for heptane is 12%, with the vast majority being less than 10%. Overall, the cup burner measurements tend to be somewhat lower than for

Table 1. Extinguishing Concentrations (Mole Fraction) of Thermal Agents

Thermal Agent	Current Work	Cup Burner [1]	Cup Burner [13]	Cup Burner [16]	Cup Burner [17]	Cup Burner [18]
Nitrogen	0.33	0.30	0.33	0.32	0.30	0.34
Argon	0.43	0.41	-	0.41	0.38	0.43
Helium	0.34	0.32	-	0.31	-	-
Carbon Dioxide	0.22	0.21	0.20	0.23	0.20	0.22
Water	0.28	-	-	-	-	-

the counterflow flame. These differences could be due to the use of different fuels or to the effects of burner configuration. The close tracking of the calculated results and the experimental findings suggests that detailed chemical kinetic modeling can accurately predict the amount of a thermal agent required to extinguish POJLDFs and cup burner flames.

The differences in the extinguishing concentrations of helium and argon seen in Table 1 are interesting since both are monatomic gases and have identical molar heat capacities. The difference is clear in both calculated and experimental values. That helium is more efficient means that at least one other parameter, in addition to heat capacity, is important for determining extinguishing efficiency. A related observation was reported by Coward and Hartwell for the inerting of premixed flames which was attributed to the much higher thermal conductivity of helium which distributes the heat of combustion over a larger region of space and therefore weakens the flame [19]. The same explanation is likely valid for diffusion flames. Sheinson et al. reached the same conclusion [1].

An important advantage of modeling investigations is the ability to perform calculations for conditions which are not physically attainable in order to learn details concerning the role of various parameters. One question which has been the subject of speculation is the relative importance of heat extraction and dilution on the effectiveness of a thermal agent. To obtain insights into this behavior, an artificial agent was created by starting with argon and setting its heat capacity to zero. Direct comparison with the results for air diluted with argon allows the relative roles of heat extraction and dilution to be characterized. Sheinson et al. have discussed the effects of dilution on extinguishment [1]. They concluded that such effects are relatively small compared to direct heat removal due to heat capacity for the thermal agents CF_4 and SF_6 .

Figure 2 is a plot of T_{max} versus exit velocity for the zero-heat-capacity argon added to air. This species decreases the strength of the flame as indicated by a reduction of T_{max} at extinction, but its effect is much smaller than for argon. The extinguishing concentration is estimated as 73%, or roughly 1.7 times the amount required for argon. This corresponds to an oxygen concentration of 5.7%. Assuming that the effects of heating an inert and dilution are additive and linear in concentration, the effectiveness of Ar as a thermal agent is estimated to be 59% due to dilution and 41% due to heat extraction. Comparison of the detailed flame structures for methane flames in air and in air diluted with zero-heat-capacity argon shows that the reason for the weakening of the flame burning in the diluted air is the passage of more oxygen through the flame to the fuel side. The unreacted oxygen which leaks through the flame front acts as a thermal agent.

One of the goals of this work was to test whether the effectiveness of a thermal agent depends on the location, relative to the high temperature flame zone, where heat extraction occurs. A surrogate thermal agent, X, was used for this purpose. The molecular weight, thermodynamic properties, and transport properties of X are identical to those of argon, but it can react unimolecularly in the presence of ambient gases to generate a new species, Y, i.e.,



Y is also very similar to argon, the only difference being that its heat of formation is assigned an arbitrary positive value instead of being zero. As a result, when Reaction (2) takes place it extracts heat and cools the local surroundings by an amount equal to the heat of reaction, $\Delta H_{X \rightarrow Y}$. Since X and Y do not react with any other species, the reaction is simply a heat sink, and therefore meets the definition of a thermal agent.

The rate constant for Reaction (2) is expressed as

$$k_{X \rightarrow Y} = A T^\beta e^{-E_a/RT}, \quad (3)$$

where A is the pre-exponential factor, β is the temperature exponent, E_a is the energy of activation, R is the gas constant, and T is temperature. By varying the parameters A , β , and E_a it is possible to change the rate and temperature range over which the reaction occurs and hence the location relative to the flame zone for heat extraction. For the calculations which follow, initial values were maintained for A and β , and only the value of E_a was changed in order to vary $k_{X \rightarrow Y}$.

Figure 3 compares calculated flame temperature versus distance from the fuel exit for two flames having exit velocities of 25 cm/s and with 5% X added to the air. For each $A = 1 \times 10^{10}$ cm³/(mole-s), $\beta = 0$, and $\Delta H_{X \rightarrow Y} = 96.1$ kJ/mole. The only difference between the two calculations is the value of E_a which equals 25.1 kJ/mole for one and 50.2 kJ/mole for the other. For the lower E_a , X begins to react immediately upon leaving the oxidizer exit which results in the temperature drop evident on the oxidizer side in Fig. 3 for positions well removed from the flame zone. When the E_a is increased to 50.2 kJ/mole the conversion of X to Y is very slow at room temperature, and there is no significant drop in temperature in the ambient region of the flow. However, as the temperature increases, X begins to convert to Y, and heat is absorbed in the higher temperature flame regions. Interestingly, T_{max} are identical within the minor variations observed in the calculations. Since flame extinguishment depends primarily on this parameter, it is concluded that the effectiveness of a thermal agent is independent of the spatial location where the heat extraction occurs as long as the gases are convected into the flame zone.

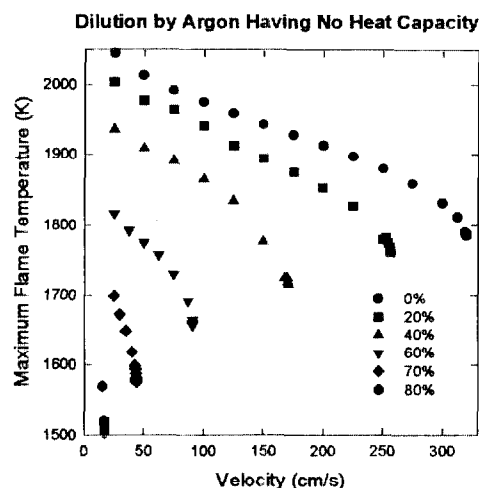


Figure 2. The maximum flame temperature is plotted versus exit velocity for a fictitious thermal agent identical to argon, except for its heat capacity which is set to be 0 J/mole-K.

A complete set of calculations was carried out for X having $\Delta H_{X \rightarrow Y} = 96.1$ kJ/mole and $E_a = 41.8$ kJ/mole. The extinguishing concentration for X is estimated to be 16%. The corresponding value for argon was 43%. Thus the heat extracted by the reaction of X to Y has reduced the amount of agent required by nearly 2/3. The effect of doubling the heat absorbed by X was considered by running a series of calculations for $\Delta H_{X \rightarrow Y} = 192.1$ kJ/mole. From these results the extinguishment concentration for X with the higher heat absorption was estimated as 9.7%. This value is roughly 60% of that found with $\Delta H_{X \rightarrow Y} = 96.1$ kJ/mole, or 20% higher than would be expected if flame extinguishment was dependent solely on the amount of heat extracted.

The role of dilution has implications with regard to estimates of extinguishing efficiency for thermal agents which are often obtained by taking ratios of heat capacities for various gaseous agents. If the agents have a large heat capacity difference, and the percentages required for extinguishment therefore differ substantially, a simple linear dependence on heat capacity should not be observed. In fact, the agent having the largest heat capacity should be less effective than expected, as observed in the current calculations.

4. Summary

It has been shown that detailed chemical kinetic modeling can be used to make quantitative predictions of the amount of a thermal agent required to extinguish a fire. Comparison of the calculated and cited experimental results suggest that minimum characteristic strain rates in fires are on the order of a few tens of inverse seconds, corresponding to a POJLDF exit velocity of roughly 20 cm/s, and that T_{max} at extinction for the extinguishing condition is approximately 1550 K. The use of surrogate agents has revealed that dilution effects are due to an increase in the amount of O_2 bleeding through the flame front and that the role of dilution is relatively small as compared to heat absorption for all but monatomic species. The location of the heat absorption relative to the flame front does not affect the ability of a thermal agent to extinguish a flame as long as the agent is convected to the flame zone. While good qualitative estimates of flame extinguishing effectiveness can be obtained based solely on the ability of an agent to absorb heat, the estimates are not perfect due to dilution effects.

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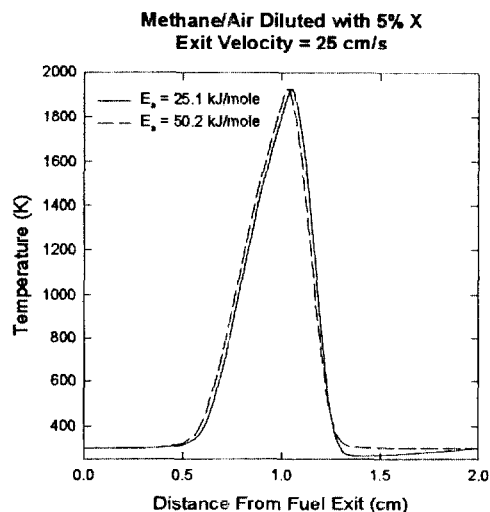


Figure 3. Calculated temperatures are plotted versus distance from the fuel exit for a methane flame burning in air diluted with 5% of a surrogate thermal agent X which can absorb heat by reacting to form Y. Results are shown for $E_a = 25.1$ kJ and 50.2 kJ.

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